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REPORT NO. 8

ANNUAL REPORT
OF
PROGRESS ON INVESTIGATIONS OF CONFECTIONERY FATS

Period Covered: June 1, 1962 - May 31, 1963

Southern Utilization Research and Development Division
Oilseed Crops Laboratory
New Orleans, Louisiana

United States Department of Agriculture
Agricultural Research Service
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Progress on Investigations of Confectionery Fats

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FOREWORD

This report describes the work of the research team composed of the Fellow of the National Confectioners Association, chemists of the Oilseed Crops Laboratory, engineers of the Engineering and Development Laboratory, and some members of Spectroscopy Investigations, Cotton Physical Properties Laboratory. Each member of the team is in charge of or responsible for one or more phases of the work.

The Fellow of the National Confectioners Association participated in the research toward developing a process for making cocoa butter-like fats by simple esterification and toward developing the procedure for tempering confectionery fats by mechanical working (Sections A and D) and assisted in modifying the method of analyzing confectionery fats (Section C). The present Fellow is Miss Betty Louise Bradshaw.

The research and development work described in this report is being carried out with the encouragement and support of the National

Confectioners Association, its Research Advisory Committee, and the member firms of the Association. Thanks are expressed for their interest, encouragement and support.

Report prepared by:

R. O. Feuge, Head
Edible Oils Investigations

Recommended by:

L. A. Goldblatt, Chief
Oilseed Crops Laboratory

Approved by:

C. H. Fisher, Director

SUMMARY

Further work was conducted on a new procedure for making cocoa butter-like fat. This procedure which consists of directly combining partial glycerides and fatty acids (esterification) is potentially capable of a 100% yield of product; that is, all of the fat formed should resemble cocoa butter. In practice, the water which is generated when partial glycerides and fatty acids are combined acts as a rearrangement catalyst and some rearrangement of the cocoa butter-like fat occurs. However, some relatively good products have been prepared in the laboratory. Up to 85% of the fat resulting from the reaction was similar to that found in cocoa butter.

The different modifications of the new procedure for producing cocoa butter-like fats investigated during the current year are described in the report. While the process as presently envisioned is sound, further substantial improvements are anticipated.

The older, previously described process for making cocoa butter-like fat by the random rearrangement of completely hydrogenated cottonseed oil and a triolein product, followed by fractionation, was further investigated in the Engineering and Development Laboratory with the objective of simplifying the process. As reported last year, the process yields a relatively good but expensive fat. The results obtained in the Engineering and Development Laboratory indicate the cost of the fat can be reduced.

An analytical procedure for determining quantitatively for the first time the contents of trisaturated and mono-, di-, and triunsaturated triglycerides in fats was evaluated and modified to particularly adapt it to the analysis of cocoa butter and similar fats.

The process of tempering cocoa butter and chocolate by intense mechanical working was further investigated. The discovery was made that liquid fat cooled quickly to below its highest melting point (supercooled liquid) could be converted readily to the highest melting crystal form (tempered) by intense mechanical working. The presence of liquid crystals in the melted fat is believed to make this possible.

The linear contraction of cocoa butter on molding and solidification was investigated. Seeded cocoa butter was found not to contract on solidification. Contraction commenced only when the bulk of the solidified fat started to change from the second highest to the highest melting form. Contraction ceased when the conversion was half-way complete. Maximum linear contraction was about 2%.

REPORT

A. Cocoa Butter-Like Fats by Simple Esterification

Introduction. In the last annual report a newly discovered process for making cocoa butter-like fats by the simple reaction between oleic acid and diglycerides (esterification) was described. This process, which is being patented, is potentially capable of converting all of the reactants into cocoa butter-like fat; that is, the potential yield is 100%. Prior to about a year ago, our research was directed toward making a cocoa butter-like fat by a process involving the rearrangement (interesterification) of a mixture of highly hydrogenated cottonseed oil and a triolein product, followed by fractionation of the reaction product. Theoretically, the best yield of cocoa butter-like fat by the older process could approach 42%, based on the total weight of reactants.

In the new process the reactants are heated in the presence of certain acid catalysts, preferably para-toluenesulfonic acid, and the water formed as a byproduct is removed as soon as it is formed. Even very small amounts of water if left in the reactants will catalyze random rearrangement and thus lower the yield of cocoa butter-like fat.

During the current year, the effect of manipulating the several variables in the process was investigated. This included an investigation of several possible methods of removing the byproduct water as soon as it formed. Also, the possibility of utilizing reactants other than oleic acid and diglycerides of saturated fatty acids was investigated.

Esterification of Diglycerides. As implied above, in the original discovery it was found that diglycerides of saturated fatty acids could

THE HISTORY OF THE UNITED STATES

The history of the United States is a story of growth and change. It begins with the first settlers, who came to the Americas in search of a new life. They found a land of opportunity, but also one of challenge. The early years were marked by conflict and struggle, as the settlers fought to establish a new society. Over time, the United States grew from a small colony into a powerful nation. It was a process of constant evolution, shaped by the dreams and aspirations of its people. The story of the United States is a testament to the power of the human spirit and the ability to overcome adversity. It is a story of hope and progress, of a nation that has always been looking forward.

be esterified to yield oleodisaturated glycerides, the principal components (about 80%) of cocoa butter. In a laboratory test carried out in the early stages of this investigation, pure 1,3-distearin and oleic acid were interacted and a 90% yield of oleodistearin was obtained. A process using oleic acid and diglycerides of oleic and palmitic acids should be feasible on a large scale because both reactants can be made commercially in large quantities in presently available equipment.

In Esterification 22 conducted during the current reporting period, diglycerides of palmitic and stearic acids were esterified with oleic acid (a 10% excess). The reactants, dissolved in mineral spirits, were added over a period of 2 hours to the reaction vessel to which the catalyst (para-toluenesulfonic acid, 0.4%) was added separately in three equal portions. The mineral spirits were continuously removed from the reaction zone by distillation. After the addition of the reactants, the reaction was continued for 2 hours and mineral spirits were added at a constant rate and continuously distilled off. A reaction temperature of 200° C. was maintained throughout the run. The product was purified by treatment with aqueous alkali and removal of the soaps which formed.

Analysis of the soapstock indicated that its fatty acid composition in percentage by weight was as follows: myristic, 0.2%; palmitic, 4.7%; stearic, 8.0%; and oleic, 87.1%. From these proportions of fatty acids it is evident that acidolysis or acid-acid interchange did not occur to a large extent.

The glyceride composition of the purified reaction product was determined by column chromatography. The results of this determination are recorded in Table I.

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Table I. Composition of the Esterification Products, Cocoa Butter-Like Fat No. 6, and Cocoa Butter

| Product | Type of Fat (Triglyceride), Weight % | | | |
|--------------|--------------------------------------|-----------------|-----------------|------------|
| | Trisaturated | Oleodisaturated | Dioleosaturated | Triolein |
| EP-22 | 20.7 | 56.8 | 16.6 | 6.0 |
| EP-23 | 46.2 | 35.1 | 12.2 | 6.6 |
| EP-24 | 16.5 | 68.2 | 13.9 | 1.4 |
| EP-25 | 19.8 | 60.6 | 19.6 | Negligible |
| Fat No. 6 | 12.1 | 70.0 | 17.9 | Negligible |
| Cocoa Butter | 1.5 | 80.3 | 18.2 | Negligible |

Esterification 23 was carried out in a manner similar to that used for Esterification 22, except that it was scaled up to twelve times the quantities of diglycerides, oleic acid, and solvent. Also, the length of reaction time was increased. Free fatty acid content after completion of the reaction was 11.5%. The composition of the purified reaction product, as determined by column chromatography, is recorded in Table I.

To establish whether or not the proportions of oleodisaturated and dioleosaturated glycerides in the reaction products could be increased by more rapid removal of the byproduct water, Esterification 24 was performed. Quantities of reactants were similar to Esterification 22 but the catalyst was added in two portions and the reaction was carried out for 1 2/3 hours at 180° C. followed by 2 2/3 hours at 190° C. with dropwise addition of mineral spirits. During the reaction a vacuum was maintained (5 p.s.i.g.) while dry nitrogen was passed through the reaction mixture to strip out the water formed.

Esterification 25 was similar to Esterification 24, except that a larger amount of dry nitrogen was used.

Fat No. 6 represented in the table is a cocoa butter-like product made last year by interesterification and fractionation. Several of the confectioners who examined it considered the product to be reasonably good.

On comparing the data for Esterification Products 22 and 23 (Table I), it is evident that scaling up the reaction had an undesirable effect on the composition. The content of oleodisaturated glycerides decreased from 56.8% to 35.1%. This decrease is attributed to the less efficient removal of the water formed as a byproduct. The traces of water rearranged the molecules of fat. When the reaction was again scaled back down and the water was removed even more efficiently by carrying out the reaction at subatmospheric pressure and by passing a stream of dry nitrogen through the reactants (Esterification 24), the content of oleodisaturated glycerides in the final product rose to 68.2%.

According to the compositional data in Table I, Esterification Product 24 is about as good as Fat No. 6 made by the interesterification and fractionation procedure. The latter fat was found by some confectioners to be a fairly good cocoa butter-like fat. The yield of Fat No. 6 was about 30%, but the yield of Esterification Product 24 was over 90%. Neither of the products contained as much oleodisaturated and dioleosaturated glycerides as does cocoa butter. A commercial sample of cocoa butter analyzed by column chromatography was found to contain 80.3% oleodisaturated glycerides and 18.2% dioleosaturated glycerides.

The attempt to improve upon the composition of Esterification Product 24 by conducting the reaction while even more dry nitrogen was passed through the reactants was unsuccessful for an as yet undetermined reason. The proportion of oleodistearin in Esterification Product 25 decreased to 60.6%. Possibly the increased flow of nitrogen also removed some of the catalyst or oleic acid in addition to the water which formed.

Obviously, the esterification reaction should be carried out under conditions which are even more suitable for removing water than those described above. Carrying out the reaction in a packed column may be a practical way of achieving the desired improvements. Packed columns are used in the large-scale, commercial manufacture of some products. Accordingly, a glass column 5 feet in length and suitable flasks, condensers, and fittings for use with the column were fabricated in our glass shop. The necessary heating elements and insulation were added, and the column and auxiliary equipment were installed, and trial esterifications using the column were made.

In these trials the reactants were allowed to percolate downward through the column while a stream of dry nitrogen or hydrocarbon vapor was passed in a countercurrent direction. None of the reaction products obtained were considered to be satisfactory cocoa butter-like fats. For example, one product obtained at 356° F. was found to contain only a small proportion of triglycerides. Apparently, the major trouble was the short reaction time in the column. It was estimated that the residence time was about 5 minutes for the bulk of the reactants. Carrying out the reaction in a continuous manner in a column may still be a good idea, but the other conditions must be changed drastically.

In another attempt to devise a procedure suitable for large-scale use, a reaction of several hours duration was carried out far below atmospheric pressure (1 mm. of mercury) and at a temperature of 356-392° F. A vaporized hydrocarbon introduced into the reactants at a higher pressure provided very vigorous agitation and helped remove the water which formed. It should be possible to modify the procedure so that only a few pounds of hydrocarbon are used per 100 pounds of reactants. The analysis of the first product which was prepared has not yet been completed.

Esterification of Monoglycerides. Instead of using oleic acid and diglycerides of saturated fatty acids in the esterification procedure it should be possible to use mono-olein and saturated fatty acids. The last-mentioned starting materials might be preferred because of their lower total cost for a given yield of product. Two series of tests with mono-olein were conducted. Stearic acid rather than a mixture of stearic and palmitic acids was used as the other reagent in order to simplify the subsequent analyses.

In the first series of experiments, stearic acid was placed in the reaction flask and mono-olein was added slowly, after which the reaction was continued until triglycerides were formed. Four reactions of this type were carried out, the main variable being the reaction temperature employed. The crude products were purified by the usual process used to refine crude vegetable oils, and the refined products were then analyzed. Three of the refined products were fractionated by partial crystallization from a light hydrocarbon, and the fractions were analyzed. The fourth refined product was fractionated by successive

crystallization from acetone, and the fractions were analyzed. All of the purified reaction products were examined dilatometrically, and all of the products were analyzed by paper chromatography. From these analyses estimates were made as to the composition of the products. The best product obtained was estimated to have the following composition:

| | |
|--------------------|-------|
| Tristearin..... | 18% |
| Oleodistearin..... | 59% |
| Dioleostearin..... | 23% |
| Triolein..... | Trace |

The oleodistearin and the dioleostearin are representatives of the monounsaturated and diunsaturated triglycerides of which cocoa butter is composed. According to one group of investigators, a sample of cocoa butter they analyzed had the following composition:

| | |
|------------------------------|-------|
| Trisaturated glycerides..... | 2.5% |
| Monounsaturated..... | 76.8% |
| Diunsaturated..... | 20.7% |
| Triunsaturated..... | 0.0% |

In a second series of experiments, a relatively high temperature was used. Stearic acid was placed in the reaction flask; the catalyst, para-toluenesulfonic acid, was added; and the vessel was heated to 374-392° F. Mono-olein dissolved in dry mineral spirits was added continuously over a period of 2 hours. Then additional catalyst was added and the reaction was continued for an additional hour while vaporized hydrocarbon was bubbled through the reaction product.

The product from one of the experimental runs, EP-18, carried out essentially as described, was refined to remove unreacted fatty acids and catalyst. The refined product was fractionated by partial crystallization from solvents. Iodine values of the product and fractions

were determined, and dilatometric examinations were made of the product and fractions. The refined product also was examined by a new column chromatography technique which will be described later. On the basis of the data obtained by the three methods of analysis it was concluded that the product contained about 60% oleodisaturated and about 20% each of trisaturated and dioleosaturated triglycerides. In other words, the proportion of cocoa butter-like fat could have equalled about 80%.

On the basis of the data from this run and from the runs in the first series of experiments one can conclude that conducting the reaction entirely at a high temperature does not increase the yield of oleodisaturated triglycerides; that is, the amount of unwanted side reaction is the same. In the first series of runs the reaction was started at a low temperature and then was increased to a high level during the later stages of esterification.

The other two esterification runs, EP-20 and EP-21, were conducted in the second series of experiments in a manner similar to that just described except that the reactions were conducted entirely under a subatmospheric pressure of 100 mm. of mercury. It was hoped that the subatmospheric pressure would aid in the removal of the water produced by the esterification reaction and that the amount of hydrocarbon required to continuously and completely remove the water would be reduced, thus making the reaction more desirable for large-scale use.

In Run EP-20 some of the stearic acid distilled out of the reaction zone and was deposited in the condenser for the hydrocarbon so that

there was less than the theoretical amount for complete reaction with the mono-olein. In Run EP-21 the apparatus was modified so that the usual slight excess of stearic acid remained in the reaction zone.

Both reaction products were purified and analyzed by the new column chromatography technique with the following results:

| <u>Fraction</u> | <u>Weight Percentage</u> | |
|-----------------|--------------------------|--------------|
| | <u>EP-20</u> | <u>EP-21</u> |
| Trisaturated | 12.4 | 24.7 |
| Oleodisaturated | 59.9 | 48.4 |
| Dioleosaturated | 19.4 | 22.6 |
| Triolein | 8.3 | 4.3 |

Apparently the yields of oleodisaturated product were not increased over previous runs but the amount of hydrocarbon used during the reaction was greatly reduced due to the partial vacuum maintained during the esterification reaction.

By removing most of the trisaturated glycerides and a portion of the diunsaturated glycerides from a reaction product prepared by a procedure similar to those represented here, it should be possible to obtain a cocoa butter-like fat in a yield of about 80%. The method of preparation from monoglycerides definitely has merit.

Esterification of Glycerol. A possible modification for making cocoa butter-like fats by direct esterification consists of preparing in the same reaction vessel the diglycerides to be used in making the fats. The successful introduction of this step would eliminate the necessity of purchasing molecularly distilled diglycerides from a separate supplier. In one experiment equal moles of palmitic acid,

oleic acid, and glycerol were mixed and allowed to esterify at a low temperature and other conditions conducive to the formation of diglycerides. Then slightly more than one mole of stearic acid was added and the triglycerides were formed. Because oleic acid does not esterify as rapidly as does palmitic acid, it was hoped that monopalmitin would form predominately in the early stages of the reaction and that this would then be esterified with oleic acid to produce oleopalmitin, which would in turn be esterified to oleopalmitostearin. After the reaction product was purified by alkali refining, subjected to fractional crystallization, and iodine values of the fractions were determined, it was estimated that the reaction product consisted of 50-60% of oleodisaturated glycerides. While this was a better product than can be obtained by the conventional type of esterification, it was not deemed to be enough of an improvement to justify further tests of this particular approach.

Impeller Reaction. In another evaluation of a new approach to making cocoa butter-like fats, a series of experiments was carried out in the esterification of oleic acid and diglycerides of palmitic and stearic acids with the aid of acetic anhydride. The acetic anhydride first reacts with the oleic acid to form mixed anhydrides of oleic acid which then react with the diglycerides. Chemically these reactions are referred to as the impeller type. They have been known for many years but have not to our knowledge been used heretofore in attempts to make cocoa butter-like fats or other fats of predetermined structure and composition.

In these experiments oleic acid and acetic anhydride were mixed for 15 minutes at 212° F. The diglycerides then were added and the solution was heated and mixed for 4 hours. The reaction product was refined by the Wesson loss procedure.

Seven experimental runs were made and the data obtained in four of these are recorded in Tables II and III.

On the basis of the data recorded in Table III one can conclude that the simple, uncomplicated addition of oleic acid to the diglycerides to form a cocoa butter-like fat did not occur. In all instances a sizable proportion of acetyl-containing glycerides also were formed. However, in only one run, EP-14, did a sizable rearrangement of the diglycerides occur. In the other runs the reactions involved mostly a simple addition of oleic and acetic acids to the diglycerides. Cocoa butter-like fats could be prepared by this procedure if the presence of some acetoglycerides is acceptable. The acetoglycerides are edible.

Table II. Proportions of Reactants Used in the Impeller-Type Reactions

| Run No. | Moles of Reactants | | |
|---------|----------------------------|------------|------------------|
| | Diglycerides ^{a/} | Oleic Acid | Acetic Anhydride |
| EP-14 | 3 | 2.5 | 2 |
| EP-15 | 3 | 2.5 | 4 |
| EP-16 | 3 | 4 | 3 |
| EP-17 | 3 | 4 | 5 |

^{a/} Diglycerides of stearic and palmitic acids.

Table III. Analytical Data on Fat Products from Impeller-Type Reactions

| Product from Run No. | Glycerides | | Free Fatty Acids ^{a/} | | | Wt. % | |
|----------------------------|-----------------|-------------------------|--------------------------------|---------|-------|----------|-------|
| | Iodine Value | Acetyl Content, % | Palmitic | Stearic | Oleic | Linoleic | Other |
| EP-14 | 9.4 | 2.5 | 10.4 | 20.9 | 65.0 | 2.7 | 1.1 |
| EP-15 | 10.5 | 5.0 | 3.0 | 4.8 | 88.3 | 2.8 | 1.1 |
| EP-16 | 12.1 | 3.7 | 4.1 | 6.8 | 85.1 | 3.1 | 1.0 |
| EP-17 | 16.4 | 4.7 | 1.7 | 6.8 | 85.1 | 3.1 | 1.0 |
| Desired | 29 | 0.0 | 0.0 | 0.0 | 96.5 | 3.5 | 0.0 |

^{a/} Calculated on the total weight of free fatty acids of long-chain length.

Related Research. While the research toward developing a process for making cocoa butter-like fats was proceeding, closely related work was being carried out under another project. The procedure for direct esterification without interesterification occurring was evaluated for the preparation of mono- and diglycerides. One of the objectives was to develop processes for making at a lower cost the intermediates needed for making cocoa butter-like fats. The esterifications were carried out with para-toluenesulfonic acid as catalyst and with the continuous removal of the water of esterification by azeotropic distillation. The effect of such variables as unsaturation, chain length, mode of addition of solvent, and reaction temperature on the composition and yield of glycerides was established. The composition and configuration

of the glycerides and the composition of their component fatty acids were determined by chemical and physical analyses. Simple esterification of 1-monostearin with oleic acid at 80° C. yielded as much as 72.3% diglycerides, and esterification of glycerol with stearic acid at 100° C. yielded up to 70.1% monoglycerides, each calculated on a glyceride basis.

B. Further Evaluation of Process for Making Cocoa Butter-Like Fat by Interesterification and Fractionation

As shown in previous reports, a reasonably good cocoa butter-like fat can be made by interesterifying 75 parts of completely hydrogenated cottonseed oil and 25 parts of olive oil or triolein product and then fractionating the reaction product to isolate the oleodisaturated glycerides. Cocoa Butter-Like Fat No. 6, described in last year's report, was made by this process. This fat had a number of desirable properties, including good gloss and hardness and a sharpness of melting which in some respects were better than that of cocoa butter. Among the disadvantages were lack of contraction on molding and relatively high cost. The latter might be reduced by changes in the process for making the fat.

To develop more data on the process, a large pilot-plant run was carried out by the Engineering and Development Laboratory. The specific objectives were to prepare a sufficient quantity of reaction product to conduct crystallization experiments with a laboratory-scale votator and to obtain data relating yield, quality of product, rate of crystallization, and rate of filtration.

Part of the reaction product was treated by the heretofore described process; that is, dissolved in acetone (1:4 by weight), cooled to 68° F., filtered, cooled to 33° F., and filtered again. This yielded 41.5% saturated fats (first precipitate) and 27.9% crude cocoa butter-like fat (second precipitate).

Cooling rate experiments conducted in the laboratory indicated that cooling the fat-acetone solution from 128° F. to 63° F. in less than 2 minutes produced crystals of saturated fat which filtered faster than similar crystals produced in the pilot plant by reducing the temperature over a period of 68 minutes and holding the mixture at the low temperature for 110 minutes before filtering. Thorough washing of the laboratory precipitate with cold acetone reduced its iodine value from 17.6 to 6.3. The precipitate obtained in the pilot plant had an iodine value of 4.3. These data indicate that rapid cooling is suitable for separating the saturated fraction.

Test data obtained on rapidly chilling to 34° F. the filtrate from the first precipitate indicated a holding time of about one-half hour is necessary to completely crystallize the cocoa butter-like fraction. Filtration rates of the slurry were slower than the corresponding rates obtained in the pilot plant. Iodine values of the cocoa butter-like fraction obtained in the laboratory ranged between 26.6 and 29.7, while that of the same fraction prepared in the pilot plant was 28.6, indicating the products to be equivalent. Addition of a crystal modifier decreased the holding time required for the second crystallization to less than two minutes.

In the last crystallization step used in making a fat similar to No. 6, a partial crystallization from commercial pentane is carried out. The mixture is cooled slowly to the desired temperature and held at this level for an hour or more.

The engineering studies indicated that commercial hexane, which is cheaper and easier to handle than commercial pentane, can be used in place of the pentane. It also was found that addition of a crystal modifier, Votator Modifier No. II, permitted shortening of the crystallization time to 60 seconds. This should make possible the use of a continuous process in place of the batch process envisioned heretofore for this step. The continuous process should be cheaper and faster.

It is planned to modify a votator for continuous operation in the pilot plant and to conduct tests with this votator toward developing a commercial process for producing a cocoa butter-like fat.

C. Analysis of Confectionery Fats

The analysis of confectionery and other fats in terms of their contents of trisaturated, and mono-, di-, and triunsaturated triglycerides has been an important problem for many years. In the past a number of relatively unsatisfactory methods of making this analysis have been employed. Very recently a far superior method has been developed.

This method for the separation of triglycerides according to their unsaturation was developed by Dr. B. deVries and reported by him in Chemistry and Industry (June 16, 1962, pages 1049-1050). The method

is simple and relatively quick. In applying it to our cocoa butter-like fats we have been able to determine quantitatively their contents of trisaturated, oleodisaturated, dioleosaturated glycerides and triolein.

The procedure consists essentially of putting the fat sample on a column of silicic acid impregnated with silver nitrate. The sample is washed through the column with solutions of petroleum ether and benzene and a solution of petroleum ether and diethyl ether. Not all of the details of the method were given by Dr. deVries in his publication. They were obtained from him by private communication. Also the method had to be adapted to our particular problem by trial-and-error experimentation.

In using the column the trisaturated glycerides appear first. It was found that while they appeared as a group, the first glycerides to appear were relatively rich in stearic acid, apparently in the form of palmitodistearins. The trisaturated glycerides which appeared during the latter part of the elution of this group were relatively rich in palmitic acid.

During the elution of the oleodisaturated glycerides, those which appeared first in this group again contained a relatively high proportion of stearic acid, compared with their content of palmitic acid. The last appearing members of the group were richer in palmitic acid. Also, any linoleodisaturated glycerides tended to appear during the latter part of the elution of this group.

Because diglycerides of palmitic and stearic acids are impurities which might occur in cocoa butter-like fats made by interesterification, diglycerides made from completely hydrogenated lard were analyzed by

the column chromatography technique. Of these saturated diglycerides, 12.1% appeared as trisaturated, 14.4% as oleodisaturated, 61.4% as dioleosaturated, and 22.8% as triolein. Obviously, any cocoa butter-like fats analyzed by this new procedure must be free of saturated diglycerides.

The chromatographic procedure which has been described is considered to be an important and valuable tool for those who need to determine the composition of confectionery fats. A description of the method as used on confectionery fats can be obtained from us on request.

D. Tempering Confectionery Fats by Mechanical Working

One of the phases of our research which was stressed last year and on which additional work has been performed this year is the tempering of confectionery fats and fat-containing confections by mechanical working. It was discovered that solid confectionery fats, which can exist in as many as four crystal forms, each having a distinct melting point, can be brought quickly to the highest melting form by intense mechanical working of the crystals. X-ray diffraction patterns, melting data, hardness, and various physical properties obtained for worked and unworked samples of fat and chocolate provided proof that the transformation in crystal form did occur. This newly discovered tempering technique is believed to be applicable to any confectionery fat which can be tempered by conventional means.

The practical value to the confectionery industry of this newly discovered technique is believed to be great. Through its use, improvements in the manufacture of chocolate and chocolate-type

confections should be possible. The use of tempering kettles might be eliminated, enrobing machines might be simplified, and the problem of maintaining just the right temper in the chocolate or confectionery coating at the time of enrobing should be reduced or eliminated. It is envisioned that in a process making use of the discovery, crushed or granulated chocolate would be fed continuously into a heat exchanger where chocolate would first be melted and then cooled until some unstable fat crystals formed. This mixture would then be forced through a series of orifices and pumped to the enrober or molding machine. Possibly only a portion of the flow to the latter machines might be forced through the orifices.

The new tempering process, which is covered in an application for a public service patent, has been described in two articles published during the past year. Reprints of the more technical of the two articles are available on request.

At the suggestion of several confectioners, including members of the National Confectioners Association, additional research on the tempering process has been conducted during the current year. This work is considered to be an extension of that reported last year. Primarily, the new work was conducted to establish the temperature limits and other variables over which the invention could be practiced.

The results obtained were unexpected in that the amounts of solid fat found to be necessary to practice the invention were small indeed. In fact, the amount of solid fat needed in a quickly chilled mixture could be so small as to be invisible to the naked eye. The only requirement was that the temperature of the quickly chilled fat subjected to

mechanical working be below and remain below the melting point of the highest melting crystal form. In other words, the liquid fat had to be supercooled.

That a liquid, supercooled fat can be converted quickly and completely into its highest melting crystal form by intense mechanical working probably is explained by the fact that liquid crystals or minute crystal nuclei of lower melting polymorphs exist in the supercooled liquid. Mechanical working converts these centers into minute crystals of the highest melting polymorph by slipping their component molecules into the most compact and dense form. These minute crystals serve as seed for the remainder of the solidifying liquid. The existence of liquid crystals in a fat even at a temperature a few degrees above the melting point of the highest melting polymorph has been described in the literature on fats and oils. The presence of these liquid crystals was revealed on examining the melted fat under a microscope with polarized light. Also, the presence of liquid crystals or crystal nuclei in liquid cocoa butter a few degrees above the melting point of some of its polymorphs has been revealed by viscosity measurements conducted at different pressures. The viscosity was found to change with pressure.

In our investigation of tempering by mechanical working, a number of different fats were used, and the temperatures at which the working was most effective were established. The degree of working required was determined. Incidentally, mechanical working is required; pressure alone was found to be ineffective. The amount of worked fat needed to satisfactorily seed unworked fat also was

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established. The details of the investigation and the data obtained will be assembled in a manuscript which will be submitted for publication in a technical journal.

E. Solidification of Cocoa Butter

Cocoa butter and chocolate exhibit on solidification under optimum conditions a sizable contraction. Thus, these products ordinarily are easy to demold. As mentioned before, our cocoa butter-like fats similar to Fat No. 6 were found to contract an insufficient degree on solidification. This made demolding difficult under some conditions. The reasons for this lack of contraction were not readily apparent, and changes in solidification techniques resulted in little improvement. Naturally, the question was asked what makes cocoa butter contract. The answer could not be found on examining the literature on the fundamental physical properties of cocoa butter. Not even a quantitative comparison of the contraction of cocoa butter and the cocoa butter-like fats could be made because values on the actual amount of linear contraction of cocoa butter could not be found in the literature.

An investigation was undertaken to determine the actual amount of contraction of cocoa butter on solidification under various conditions and to develop a theoretical explanation for this contraction. A special volumetric dilatometer which permitted the rapid heating and cooling of a small sample was devised and used in the investigation. Also used was a special aluminum mold fitted with passageways through which water was circulated to quickly change and then accurately

maintain the temperature of the sample in the mold. The contraction of the molded sample, which measured approximately 1 inch in length by 1/4 inch in width by 1/8 inch in thickness, was measured by observation through a microscope having a calibrated scale in the eyepiece.

When an aged sample of cocoa butter was heated to 120° F. to destroy all crystals and a portion of the sample was poured into the mold and quickly solidified by cooling to 61° F., practically no contraction in the mold was observed, even after several hours. Also, the sample remained almost entirely in the lower melting crystal forms or polymorphs.

Tests were conducted to establish at what temperature the highest melting crystal form of cocoa butter is destroyed so that on subsequent solidification insufficient seed crystals of this form are present to ensure effective conversion of the whole mass to the highest melting form. For the particular sample of commercial cocoa butter under test, the maximum temperature of the melt could not exceed 95° F.

In other tests it was found that when melted cocoa butter has been adequately seeded with crystals of the butter in the highest melting form and the temperature is lowered to several degrees below the melting point of this form, very slow solidification occurs. From this it can be concluded that solidification from the melt directly to the most stable form is not an important factor in the commercial processing of cocoa butter and chocolate.

To obtain the best contraction on the solidification of cocoa butter, the melt must be cooled to below 95° F., seeded with cocoa butter in the highest melting form, and then the mass must be solidified

quickly so that most of the fat crystallizes in the second highest melting form. The optimum temperature for the particular cocoa butter examined was approximately 61° F. At this temperature the maximum linear contraction was about 2%.

Contraction did not occur during or immediately after solidification. The bulk of the contraction occurred between the 5th and 15th minute after solidification. When contraction in the mold started, the second highest melting form predominated; and contraction stopped when about one-half of this form had been converted into the highest melting form.

The experimental data which were developed, when coupled with the idea of rigid particles growing in a relatively plastic mass, serve well to explain why cocoa butter contracts after molding under conditions used in the confectionery industry. When cocoa butter seeded with crystal nuclei of the highest melting polymorph solidifies at about 61° F., the immediate effect is the formation of a large amount of the second highest melting form. Each nucleus of the highest melting form starts to grow as soon as the second highest melting form is present. As the content of the highest melting form increases, the whole mass contracts because the density of this form is greater than that of the second highest melting form and the latter form is relatively plastic. When the crystallization centers of the highest melting form meet, linear contraction ceases for practical purposes.

